

Polymers with self-attraction and stiffness: a generic phase structure

J. Krawczyk,^{*} A. L. Owczarek,[†] and T. Prellberg[‡]

*School of Mathematical Sciences, Queen Mary, University of London,
Mile End Road, London E1 4NS, United Kingdom and*

Department of Mathematics and Statistics, The University of Melbourne, 3010, Australia

Recently it has been shown that a two-dimensional model of self-attracting polymers based on attracting segments displays two phase transitions, a θ -like collapse between swollen polymers and a globular state and another between the globular state and a polymer crystal. On the other hand, the canonical model based on attracting monomers on lattice sites displays only one: the standard tricritical θ collapse transition. Here we show that by considering both models with the addition of stiffness the two models display the *same* generic phase diagram. In fact we claim that any two-dimensional model of a self-attracting single polymer in solution based upon a fully volume-excluded backbone with isotropic short range attraction should show this same phase structure. We point to the model of hydrogen bonded polymers to demonstrate this observation. In three dimensions we note that more than one crystalline phase may occur.

I. INTRODUCTION

The study of the thermodynamic behaviour of a single model molecule in solution has been re-invigorated of late with a variety of new experimental techniques able to tease out more refined features and also with an escalating interest in biopolymers. It is therefore perhaps surprising to find that alternative simple models of a single polymer display different phase structures: for some models there exist only two thermodynamic phases, a high-temperature swollen coil and a disordered liquid-like globule, whereas for other models there is a third, compact phase with crystalline order.

In this letter we present a unified description of these models, based on the study of a particular model that provides the missing link. This model incorporates attractive interactions between segments of the polymer and bending stiffness. Computer simulations allow us to conclude that all the two-dimensional models in the literature are one or two parameter slices of a larger model in which only three phases exist. We therefore *conjecture* that in any model of an isolated non-oriented polymer restricted to a substrate (so being effectively two-dimensional), with homogeneous short-ranged attractive interactions between parts of the polymer, regardless of whether these parts are single monomers or groups of monomers (so that an effective stiffness is introduced), only the three phases mentioned above will occur in the larger parameter space. The phase transition between the swollen coil and the globule is described by the traditional θ -point, while the transition between the swollen coil and the crystal is first order. Finally the most interesting transition between the globule and the crystal is second order (in two dimensions).

Background

The canonical description of the thermodynamic states of a isolated polymer has a reference high temperature disordered state known as the ‘swollen coil’ or ‘extended state’ which is described by the $N \rightarrow 0$ of the magnetic $O(N)$ model and correspondingly by the $N \rightarrow 0$ of the φ^4 $O(N)$ field theory [1]. The lattice model of self-avoiding walks is a good model of this situation where in both two and three dimensions the fractal dimension of the polymer d_f is less than the dimension of space and also less than the fractal dimension of simple random walks (which is 2). The values of $d_f = 1/\nu$, where ν is the exponent describing the scaling of the radius of gyration of the polymer with its length, are $4/3$ in two dimensions [2] and $1.702(1)$ in three dimensions, have been well studied [3]. It is expected that if the temperature is lowered then the polymer will undergo a collapse at one particular temperature, called the θ -temperature. At temperatures lower than the θ -temperature the fractal dimension of the polymer attains that of space, that is $d_f = d$. The standard description of the collapse transition is a tricritical point related to the $N \rightarrow 0$ limit of the φ^4 – φ^6 $O(N)$ field theory [4, 5, 6]. Thermodynamically this implies that there is a second-order phase transition on lowering the temperature: the specific heat exponent α is conjectured to be $-1/3$ in two dimensions [7] and 0 in three dimensions with a logarithmic divergence of the specific heat. In two dimensions the fractal dimension of the polymer is expected to be $d_f = 7/4$ [7]. The low temperature state has been likened to a liquid drop; it is compact but disordered [8]. The corresponding lattice model which displays this collapse θ -transition is the *Interacting Self-Avoiding Walk* model (ISAW) [9] where an attractive potential is associated with pairs of sites of the walk adjacent on the lattice though not consecutive along the walk.

However, more recently two other simple models of a single polymer have been studied. These have been introduced in the context of biopolymers where hydrogen bonding plays an important role [10], and the in-

^{*}Electronic address: j.krawczyk@ms.unimelb.edu.au

[†]Electronic address: a.owczarek@ms.unimelb.edu.au

[‡]Electronic address: t.prellberg@qmul.ac.uk

interacting residues lie on partially straight segments of the chain. The first one, the *Interacting Hydrogen-Bond* model (IHB) [11, 12, 13], modifies the ISAW model such that a pair of sites on the self-avoiding walk acquires a hydrogen-like bond potential if the sites are (non-consecutive) nearest neighbours, as in the ISAW model, and each site lies on a straight section of the walk. This model displays, in contrast to ISAW, a single collapse transition which is *first order* in both two and three dimensions. Here the low temperature state is an anisotropic ordered compact phase that is described as a polymer crystal.

The second model introduced to account for hydrogen bonding is the *Attracting Segments* model (AS) [14, 15, 16] (also known as ‘interacting bonds’). It is a lattice model based upon self-avoiding walks where an attractive potential is assigned to *bonds* of the walk that lie adjacent and parallel on the lattice (though not consecutive along the walk), see Figure 1. This model has been less extensively studied on regular lattices — it has been studied on the square lattice [16] — though *two* phase transitions have been identified, one of which is identified as the θ -point.

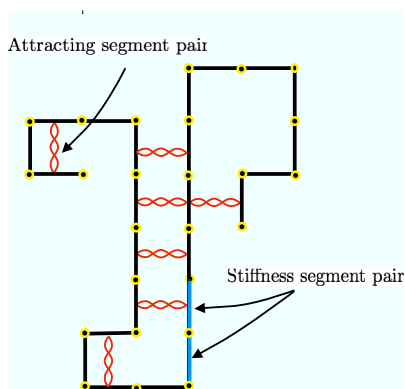


FIG. 1: A self-avoiding walk with the interactions of the attracting segment (AS) model shown as intertwined curves between bonds of the walk on opposite sides of the squares of the lattice. Also shown is an example of a stiffness segment pair which obtains a stiffness energy in our generalisation.

Crucially, there is a different modification of the ISAW model that displays two phase transitions for a range of parameters, namely the *semi-flexible* ISAW model [17, 18, 19]. Here two energies are included: the nearest-neighbour site interaction of the ISAW model and also a stiffness energy associated with consecutive parallel bonds of the walk (equivalently, a bending energy for bends in the walk). This has been studied on the cubic lattice by Bastolla and Grassberger [17]. They showed that when there is a strong energetic preference for straight segments, this model undergoes a single first-order transition from the excluded-volume high-temperature state to a crystalline state. On the other hand, if there is only a weak preference for straight segments, the polymer undergoes two phase transitions. On

lowering the temperature the polymers undergoes a θ -point transition to the liquid globule followed at a lower temperature by a first-order transition to the frozen crystalline phase. Recent work [20] on the semi-flexible ISAW model on the square lattice displays a similar phase diagram though the transition between the globule and the frozen state has been seen to be second order.

It would seem reasonable to conjecture that the phases and phase transitions seen in the semi-flexible ISAW model are essentially those seen in both the IHB model and the AS model. On the other hand the addition of stiffness to the IHB model has been seen to change little of the behaviour of that model [20]. Importantly, the IHB model was recently extended [21] to a hybrid model (IHB-INH) that includes both the hydrogen-like bond interactions and non-hydrogen like bond interactions, with separate energy parameters. When the non-hydrogen bonding energy is set to zero the IHB model is recovered. If both energies are set to be the same value then the ISAW *without stiffness* is recovered. They found for large values of the ratio of the interaction strength of hydrogen-bonds to non-hydrogen bonds, that a polymer will undergo a single first-order phase transition from a swollen coil at high temperatures to a folded crystalline state at low temperatures. On the other hand, for any ratio of these interaction energies less than or equal to one there is a single θ -like transition from a swollen coil to a liquid droplet-like globular phase. For intermediate ratios two transitions can occur, so that the polymer first undergoes a θ -like transition on lowering the temperature, followed by a second transition to the crystalline state. In three dimensions it was found that this second transition is first order, while in two dimensions they found that it is probably second order with a divergent specific heat. In other words, by adding an energy to both the hydrogen-like and non-hydrogen like interactions a phase diagram similar to the one for the semi-flexible ISAW is found. We note that the IHB model has been generalised on the cubic lattice in such a way that two different crystalline phases were observed [13].

Here we bring together the pieces of this puzzle by studying the AS model in the presence of stiffness on the square lattice. We concentrate our study in two dimensions where only one type of crystalline phase has been observed.

Semi-flexible Attracting Segments model

Our semi-flexible attracting segments model (semi-flexible AS model) is a simple self-avoiding walk on square lattice, with self-interactions as in the AS model [14, 15, 16] and a stiffness (or equivalently bend energy) added. Specifically, the energy of a single chain (walk) consists of two contributions (see Figure 1): the energy $-\varepsilon_{as}$ for each attracting segment pair, being a pair of occupied bonds of the lattice that are adjacent and parallel on the lattice and not consecutive along the walk; and an energy $-\varepsilon_{ss}$ for each stiffness segment pair, being a pair of bonds consecutive along the walk that are parallel. A

walk configuration φ_n of length n has total energy

$$E_n(\varphi_n) = -m_{as}(\varphi_n) \varepsilon_{as} - m_{ss}(\varphi_n) \varepsilon_{ss}, \quad (1)$$

where m_{as} denote the number of attracting segment pairs and m_{ss} denotes the number of stiffness segment pairs. The partition function is defined then as

$$Z_n(\beta_{as}, \beta_{ss}) = \sum_{m_{as}, m_{ss}} C_{n, m_{as}, m_{ss}} e^{\beta_{as} m_{as} + \beta_{ss} m_{ss}}, \quad (2)$$

where $\beta_{as} = -\varepsilon_{as}/k_B T$ and $\beta_{ss} = -\varepsilon_{ss}/k_B T$ for temperature T and Boltzmann constant k_B . $C_{n, m_{as}, m_{ss}}$ is the density of states, which we have estimated by means of Monte Carlo simulations.

II. RESULTS

On the square lattice we performed simulations using the FlatPERM algorithm [22], estimating the density of states up lengths for $n = 128$ over the two parameters m_{as} and m_{ss} . We have also estimated the end-to-end distance as a measure of the size of the polymer: this enables us to estimate the fractal dimension of the polymer via estimation of the exponent ν . The density of states allows us to calculate the internal energy and the specific heat, or equivalently, the mean values and the fluctuations of m_{as} and m_{ss} , respectively. This allows to locate phase transitions through the possible divergences in the specific heat. To detect orientational order, we estimated the *anisotropy parameter* [17]. In two dimensions, denoting the number of bonds parallel to the x -, and y -axes by n_x and n_y , respectively, we define

$$\rho = 1.0 - \frac{\min(n_x, n_y)}{\max(n_x, n_y)} \quad (3)$$

to be the anisotropy parameter. In a system without orientational order, this quantity tends to zero as the system size increases. A non-zero limiting value less than one of this quantity indicates weak orientational order with $n_{min} \propto n_{max}$, while a limiting value of one indicates strong orientational order, where $n_{max} \gg n_{min}$.

Figure 2 shows the peak positions of the fluctuations in m_{as} and m_{ss} at length 128 from simulations on the square lattice. It is clear from shorter lengths that some of these peaks are asymptotically diverging. We therefore have a finite-size approximation to a phase diagram in this figure.

To characterise the possible phases in each region we have considered the scaling of the end-to-end distance. For small β_{as} we find that the exponent ν is close to $3/4$: specifically we find $d_f = 1.33(1)$ for $(\beta_{as}, \beta_{ss}) = (0.5, -0.5)$. On the other side of the first curve separating small β_{as} from larger β_{as} we find that ν is close to $1/2$ no matter how large β_{as} becomes: at points (β_{as}, β_{ss}) being $(1.8, -0.5)$, $(2.3, -0.5)$ and $(3.0, -0.5)$ we find $d_f = 2.00(1)$. Hence the two phases to the right of the leftmost curve are dense. To clarify the two low temperature phases we have measured the anisotropy parameter. We find that the anisotropy parameter is tending

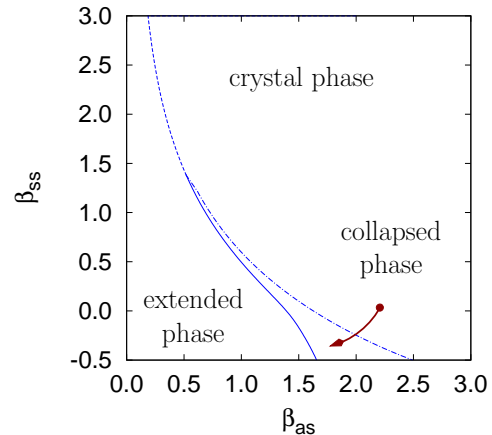


FIG. 2: Phase boundaries based upon data at length 128. The boundaries were found by looking for the maximum in fluctuation in the number of as contacts (the left boundary) and the number of ss segments (the right boundary).

to zero for values of β_{as} smaller than the right boundary and tending towards one for values of β_{as} larger than the right boundary. That is, it tends to zero in the swollen and globular phases and one in the crystal phase. In Figure 3 we show the anisotropy parameter at fixed $\beta_{ss} = 1.5$ and at fixed $\beta_{as} = 2.0$ plotted for three different polymer lengths. There are stronger corrections to scaling in the globule to crystal transition evident.

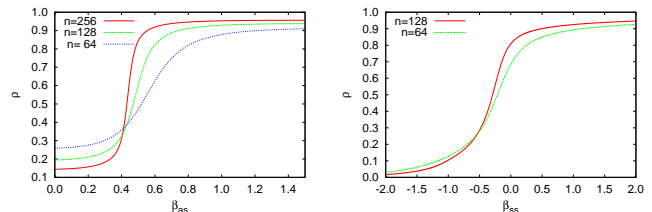


FIG. 3: The anisotropy parameter ρ for $\beta_{ss} = 1.5$ (left) and $\beta_{as} = 2.0$ (right) for polymer lengths $n = 64, 128$ and 256 . For $\beta_{ss} = 1.5$ it is converging to 0 for small β_{as} and to 1 for large β_{as} , changing over roughly at $\beta_{as} = 0.4$. For $\beta_{as} = 2.0$ it is converging to 0 for small β_{ss} and to 1 for large β_{ss} , changing over roughly at $\beta_{ss} = -0.5$.

We therefore surmise that for high temperatures the polymer is in the swollen phase, while at intermediate temperatures the polymer may be in a globular state, and for low enough temperatures always enters the anisotropic crystalline state. One can compare the finite size phase diagram that we have to that of the semiflexible ISAW model [17, 20], see Figure 4. Apart from a shift of boundaries, so that for $\beta_{ss} = 0$ there is only one phase transition, the two diagrams are remarkably similar.

To test the similarity of these diagrams further we have explored the phase transition between the phases. It has

been found that the swollen-to-crystal transition in the semi-flexible ISAW model [17, 20] is first-order in two (and three) dimensions. We find the same here for our semi-flexible AS model in two dimensions: the scaling of fluctuations of m_{as} have a classic first-order behaviour with a linear divergence in polymer length and a transition width scaling as the inverse length. The globule-to-crystal transition has been found to be second order in two dimensions. To consider the globule-to-crystal transition on the square lattice in our model more closely, we have also simulated longer length polymers up to $n = 512$ for constant $\beta_{ss} = -0.5$. Using these simulations we find results similar to those found for the semi-flexible ISAW model. The swollen-globule transition is expected to be in the universality class of the θ -point and its specific heat signature is weak ($\alpha < 0$). This is difficult to see at the lengths considered here though the transition is clearly weakening with length.

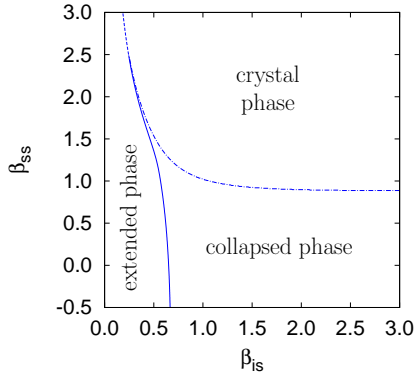


FIG. 4: Finite-size phase diagram for the square lattice semi-flexible ISAW model.

We have therefore seen that the phase diagrams of the

semi-flexible ISAW model and our semi-flexible AS model contain the same phases and phases transitions. In fact they have a very similar shape.

Finally, it is instructive to consider the phase diagram of the extended interacting hydrogen-bonding model [21]. While the different type of parameters make comparisons indirect, we note that the same phases occur and same phase transitions as the two semi-flexible models discussed in two dimensions. This supports the idea that regardless of how stiffness is introduced in the interacting polymer model, these three phases will occur in an appropriate parameter space. To make this conclusion more concrete one can realise that by enlarging the parameter space of concern in the manner considered in [15] the ISAW model, the IHB and the AS models are all specialisations of a more general model. Now we have seen that with the addition of a further stiffness parameter the general phase structure of the more general model should still only contain the three phases and phases transition discussed above.

In this article we have developed a more complete and consistent understanding of the phase structure of a single polymer in solution, and restricted to a substrate so that it is effectively two-dimensional, than had previously been available. For the three-dimensional model we expect a weaker result where more than one crystalline phase may exist. (Our preliminary studies of the AS model on the cubic lattice show that only one phase transition occurs which makes it less relevant to the discussion here: the observations may be understood as the weaker effect of AS model effective stiffness there.) It should be in this context that experimental results of polymer collapse be analysed.

Financial support from the Australian Research Council and the Centre of Excellence for Mathematics and Statistics of Complex Systems is gratefully acknowledged by the authors.

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